FABRICATION OF MIXED MATRIX MEMBRANES USING POLYIMIDE AND ZIFs FOR CO_2 SEPARATION

BY

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To

My family

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LIST OF ABBREVIATIONS

GHGs	:	Green House Gases
MOFs	:	Metal Organic Frameworks
ZIFs	:	Zeolite Imidazole Frameworks
XRD	:	X-ray Diffraction
SEM	:	Scanning Electron Microscopy
TGA	:	Thermal Gravimetric Analysis
NMR	:	Nuclear Magnetic Resonance
MMM	:	Mixed Matrix Membranes
P	:	Permeability
S	:	Solubility
D	:	Diffusivity
α	:	Ideal Selectivity

ABSTRACT

Full Name : Akram Salem Obaid Ghanem

Thesis Title : Fabrication of a Selective Mixed Matrix Membrane Using Polyimide and ZIFs For Co_2 Separation

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New mixed matrix membranes (MMMs) have been fabricated, characterized and examined in gas separation applications. The preparation of theses MMMs carried out by the blending of an inorganic filler in the polymer matrix that lead to the enhancement of gas separation performance. Two types with micro particle size of chabazite (CHA), and hydrophobic Zeolite Imidazole Frameworks (ZIF), namely ZIF-300, and ZIF-302 have been synthesized and scaled up. The resulting particles were embedded in polyimide resin (Matrimid 8512) to fabricate different loading (5 %wt, and 15 %wt) mixed matrix membranes along with pure polymeric membrane to investigate the performance toward CO_2 separation.

Different characterization techniques were utilized to investigate synthesized ZIFs and MMMs. ZIF-300, and ZIF-302 were characterized by XRD, ^{H}NMR, SEM, TGA, and Nitrogen sorption analysis. While mixed matrix membranes were characterized by XRD, TGA, SEM. Single gas permeation analysis was carried out at 4 bar and 35 ^{o}C to investigate separation performance of different MMMs. Because of high affinity of ZIFs for Carbon Dioxide, CO_2 permeability increased 112% and 130% for 5%wt MMMs compared with neat polymer. The incorporation of more filler (15% wt) enhanced CO_2 permeability to 64% and 36% compared with 5%wt MMMs, with no remarkable enhancement in N_2 and CH_4 permeability. In terms of ideal selectivity, CO_2/N_2 was increased from 19.04 to 28.06 for 5%wt ZIF-300/polyimide and 15%wt ZIF-300/polyimide respectively, and from 26.42 to 33.08 for 5%wt ZIF-302/polyimide and 15%wt ZIF-302/polyimide respectively. Even though, no significant increase in CO_2/CH_4 selectivity. For permselectivity, the increase of filler loading improved MMMs performance, in accordance to Robsen upper bound curves.

ملخص الرسالة

الاسم الكامل: أكرم سالم عبيد غانم

عنوان الرسالة: تصنيع أغشية نسيجية مختلطة باستخدام بوليمر البولي اميد والهياكل المعدنية العضوية من هياكل الزيوليت إيمدازول واستخدامها في فصل ثاني أكسيد الكربون

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: مايو 2017

اجتذبت الأغشية النسيجية المختلطة والتي يتم فيها خلط مواد عضوية مع بوليمر لزيادة وتعزيز أداء فصل الغازات اهتمام الباحثين خلال العقدين الماضيين. في هذا العمل، تم تصنيع نوعين من الهياكل المعدنية العضوية النافرة للماء من نوع هياكل الزيولايت إيميدازول (ZIF-300 و ZIF-302). تم أضافة الهياكل المصنعة إلى بوليمر من نوع راتنج بوليميد لتصنيع أغشية نسيجية مختلطة بأوزان مئوية مختلفة (5% و10% و15%) لاختبار مدى فعالية هذه الأغشية النسيجية في فصل غاز ثاني أكسيد الكربون.
تم استخدام تقنيات مختلفة لفحص خصائص الهياكل المعدنية العضوية والأغشية النسيجية المختلطة. في فحص الهياكل المعدنية تم استخدام جهاز حيود الأشعة السينية، المجهر الالكتروني، التحليل الوزني الحراري، الرنين المغناطيسي النووي، وجهاز امتزاز غاز النيتروجين. بينما في فحص الأغشية النسيجية تم استخدام جهاز حيود الأشعة السينية، المجهر الالكتروني، والتحليل الوزني الحراري. تم إجراء اختبار نفاذية الغازات عند (4 بار و35 درجة مئوية) لفحص أداء الأغشية النسيجية المصنعة. بسبب الانجذاب الشديد للهياكل المعدنية لغاز ثاني أكسيد الكربون، تم ملاحظة ارتفاع نفاذية ثاني أكسيد الكربون بنسبة 110% و130% للأغشية النسيجية ذات 5% من الهياكل المعدنية العضوية مقارنة مع البوليمر الصافي. أيضاً رفع نسبة الهياكل المعدنية في الأغشية النسيجية أدى إلى ارتفاع النفاذية بنسبة 64% و36% مقارنة مع الأغشية النسيجية المختلطة ذات 5%. بينما لم يلاحظ أي ارتفاع مذكور في نفاذية كلاً من غازي النيتروجين والميثان. الانتقائية لغاز ثاني أكسيد الكربون إلى النيتروجين ارتفعت من 19.04 إلى 28.06 لكل من 5% من نوع ZIF-300 و15% من نوع ZIF-300، وارتفعت أيضاً من 26.42 إلى 33.08 لكل من 5% من نوع ZIF-302 و15% من نوع ZIF-302. ولم يلاحظ أي ارتفاع لانتقائية غاز ثاني أكسيد الكربون إلى الميثان. لاحظنا أن زيادة نسبة الهياكل المعدنية في الأغشية النسيجية المختلطة أدى إلى تحرك الأغشية النسيجية المختلطة إلى منحنى روبسون.

CHAPTER 1

INTRODUCTION

Global warming is considered as primary environmental issue in the world due to its impacts in our life. As a phenomenon, Global warming means increasing the earth's average surface temperature as a reason of greenhouse gases GHGs (CO_2, CH_4, N_2O, water vapor, Hydrofluorocarbons HFCs, O_3) that work as a trap for the heat that escape from the earth, which reflected harmfully on the environment due to the emissions of greenhouse gases GHGs, especially for carbon dioxide CO_2 that represents the highest percentage among GHGs. The main source of these gases is fossil fuel (oil, coal, and natural gas). According to International Energy Agency (IEA) report, the concentration of CO_2 in the atmosphere reaches to high level (397 ppm) with a rate of 2 ppm/year for last decade. In addition most of CO_2 emissions came from energy sector 68% [1]. Many mitigation approaches have been conducted to reduce and control CO_2 emissions [2], such as:

1- Conservation of energy and improve efficiency.

2- Using of sustainable energy such as solar energy, wind energy, etc.

3- Using of low carbon fuels, including nuclear power, and natural gas.

4- Afforestation and reforestation approaches.

5- Carbon capture and separation.

Each approach has its advantages and limitations, some of them deals with the source of emissions such as using natural gas and clean fuel. Others deals with the energy management such as energy conservation and efficiency improvement. From all approaches that were mentioned above carbon capture and sequestration CCS considered as a new approach that can reduce the emissions of CO_2 (85 – 90%) [2].

1.1 Carbon Capture and Sequestration

Many techniques used to capture or separate CO_2. The choice of the technology is relying on the combustion type that determine the appropriate method to remove CO_2. There are mainly three processes are commercially used:

1.1.1 Pre-combustion:

Where the removal of CO_2 exists after the combustion takes place. The ability of retrofitting this process into power plant is better than others. However, the low concentration of CO_2 in the gas mixture can affect capturing efficiency.

1.1.2 Post combustion:

Pretreatment of the fuel before combustion takes place is the major difference between this process and others, the gasification of the fuel forms syngas (H_2, CO). Then, under water-gas shift reaction, CO converted into CO_2. This pretreatment leads to a high CO_2 concentration in gas mixture, as a result, high separation efficiency.

1.1.3 Oxy-fuel:

In this technique the air replaced by using a pure oxygen in the combustion, which eliminate N_2 in the exhaust gas that effects the separation process. The main disadvantage

of this process is pure oxygen that comes from a high-power consumer unit (cryogenic air separation unit). Figure 1 illustrates different CO_2 capture technologies.

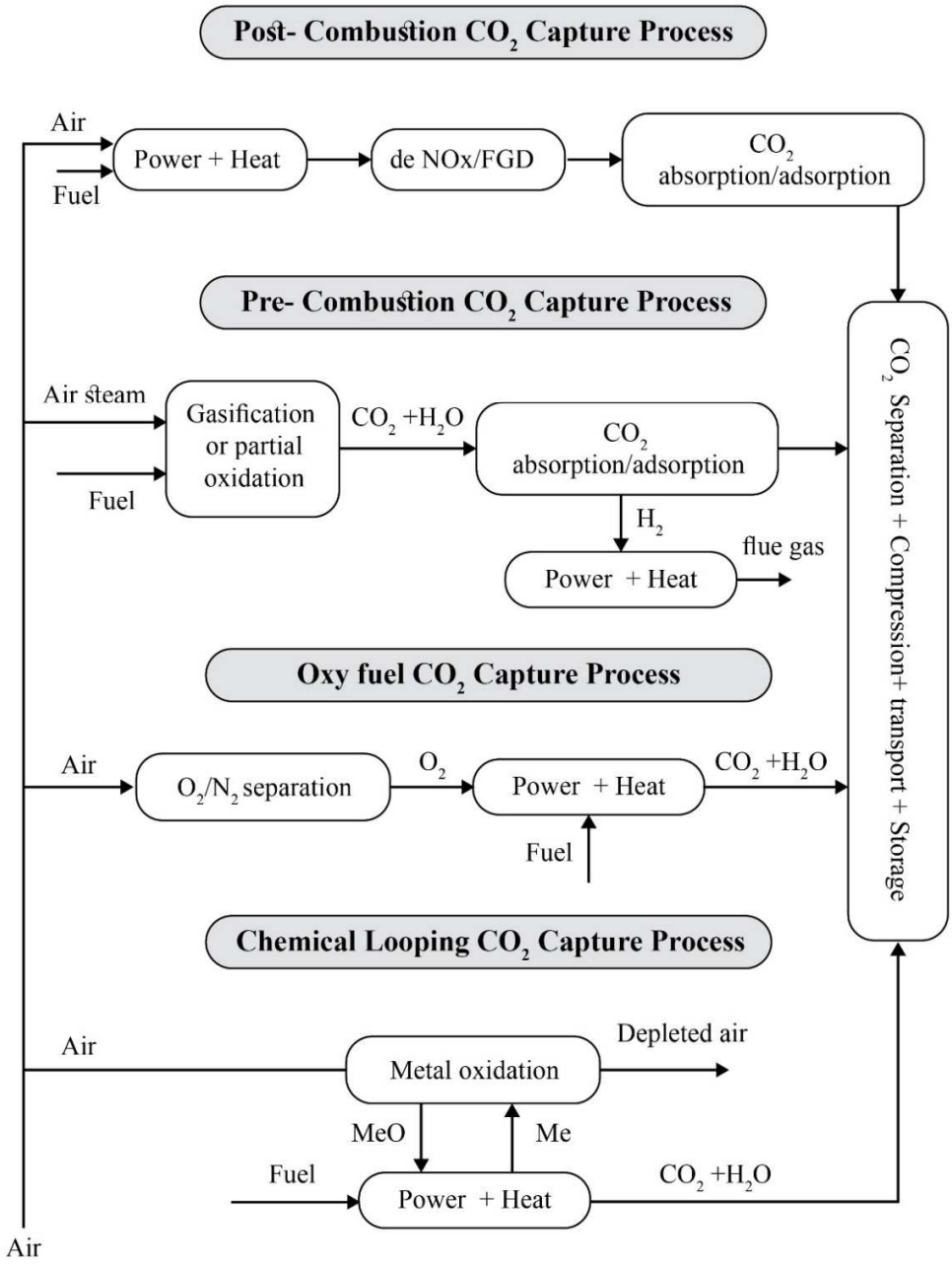

Figure 1 CO_2 capture technologies [2]

To separate CO_2 from a gas mixture (N_2/CO_2, H_2/CO_2) there are many technologies have been utilized. Figure 2 shows the schematic diagram of these technologies. Absorption where CO_2 is separated from gas mixture using liquid sorbent, such as diethanolamine (DEA). It needs huge amount of sorbent plus corrosion problems. Adsorption, a solid material with high surface area, high selectivity, and regeneration capability is used to adsorb CO_2. Many potential materials used as adsorbent such as zeolite, silica gel, activated carbon, and metal organic frameworks. Using membranes for separation of CO_2 from a gas mixture is a potential approach where polymer by allowing CO_2 selectivity to pass through it, and excluding other gases. The separation ability of membranes is higher than absorption, typical membranes such as ceramic membranes, metallic membranes, and polymeric membranes.

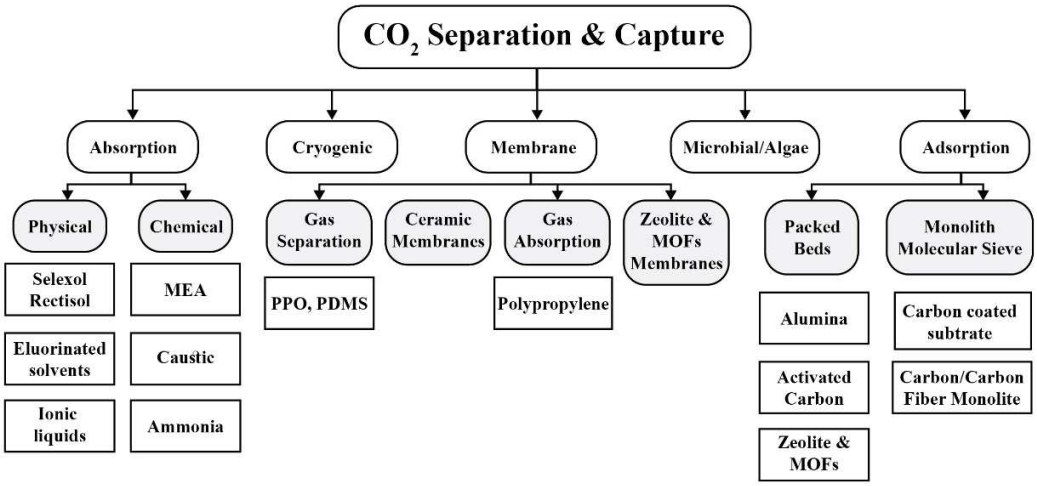

Figure 2 CO_2 Separation and Capture [3]

Cryogenic distillation applied a physical principle where the air is liquefied, then, distillated in a column based on boiling temperature. This unit ASU consumes power. Other methods used in CO_2 separation are Chemical looping combustion, hydrate-based separation. Metal organic Frameworks MOFs as a new class of material that developed last decade has a remarkable affinity to adsorb CO_2 compared with other gases. Which gave the scientists an opportunity to study the application of MOFs in CO_2 capture and sequestration.

1.2 CO_2 capture using Metal Organic Frameworks (MOFs):

Separation of carbon dioxide from post combustion units using a variety of high selective adsorbents is improved last decades. High surface area, stability, and high adsorption capacity are the main properties that make these adsorbents to be used in CO_2 capture and separation. Metal organic frameworks is a new class of material that has a metal ion and organic ligands. This extraordinary material has many features including high internal surface area, thermal stability, chemical stability, scalability, and high adsorption capacity [4]. From its discovery last two decades, MOFs were applied in different applications such as gas storage [5], catalysis [6], biomedical [7], gas capture and separation [8]. Metal organic frameworks prepared by different methods: solvothermal, Sonochemical, microwave, mechanochemical, Ionic liquids, microfluid and dry gel [9]. MOFs can be classified into rigid (fixed) or flexible. Rigid MOFs have a fixed structure, while the flexible one changes with the changing in pressure or temperature. According to literature, more than 20,000 MOFs were synthesized, and the surface area varies from 1000m^2/g to 10,000 m^2/g. The highest surface areas among MOFs are: NU-100 (6140 m^2/g) [10], MOF-210 (6,240 m^2/g)[11], MOF-200 (4,530 m^2/g)[12], MOF-205 (4,460 m^2/g)[13], PCN-80

(3,850 m^2/g)[14], IRMOF-1 (2,833 m^2/g), IRMOF-6 (2,516 m^2/g), Mg-MOF-74 (1,800 m^2/g)[15], HKUST-1 (1,781 m^2/g) [16] , etc. see table 1 shows different types of metal organic frameworks with its BET surface area.

Table 1 BET surface area of different types of MOFs

MOF	BET surface area m^2/g	Ref.
HKUST-1	1781	[16]
Mg-MOF-74	1800	[15]
IRMOF-6	2516	[15]
IRMOF-1	2833	[15]
PCN-80	3850	[14]
MOF-205	4460	[13]
MOF-200	4530	[12]
NU-100	6140	[10]
MOF-210	6240	[11]
NU-109E	7010	[10]
NU-100E	7140	[10]

Some types of metal Organic Frameworks have many problems, for example (IRMOFs) such as MOF-5, UiO-66, MOF-74, NOTT-100 severe from instability under humid environment, that leads to structure collapse. In addition, MOFs with high surface area such as MOF-210 (6,240 m^2/g), MOF-200 (4,530 m^2/g) does not work well under low pressure. However, it is useful for gas storage applications. To overcome these difficulties, there are some strategic techniques used to enhance the stability and capacity of MOFs. To improve the capacity of metal organic frameworks, functionalization is one of these choices where a high affinity for CO_2 groups introduced to MOFs such as (amine group) NH_2-MIL-

101, NH_2-MIL-53 are two examples where amino functionalization enhances the selectivity toward CO_2 comparing with un-functionalized MOFs [17][18]. Other method is metal doping where a metal cation such as Li^+ was incorporated by ion exchange or chemical reduction. Moreover, MOFs stability (thermal, chemical) enhancement is crucial, so generation MOFs from metal ions with high valence (Al-MIL-110, Cr-MIL-101), or ligands with imidazole (ZIFs) will improve the stability.

Zeolite imidazole Frameworks (ZIFs) are a sub-class of MOFs where the metal ion connected with imidazolate bridge. It is distinguished by its robustness, chemical, and thermal stability since strong interaction between metal ion and imidazole [19]. Figure 3 shows different crystal structure of ZIFs. Many structures of ZIFs with different topologies were prepared such as (ZIF-8 [20],ZIF-14 [21], ZIF-70, ZIF-71[22], ZIF-91 [23], ZIF-300, ZIF-301, ZIF-302), the last three ZIFs has hydrothermal stability among all ZIFs [24].

By taking the advantages of MOFs and polymeric membranes in gas separation performance, and mechanical properties, etc. Mixed matrix membranes where the MOFs embedded in polymer matrix is a good choice to enhance gas separation.

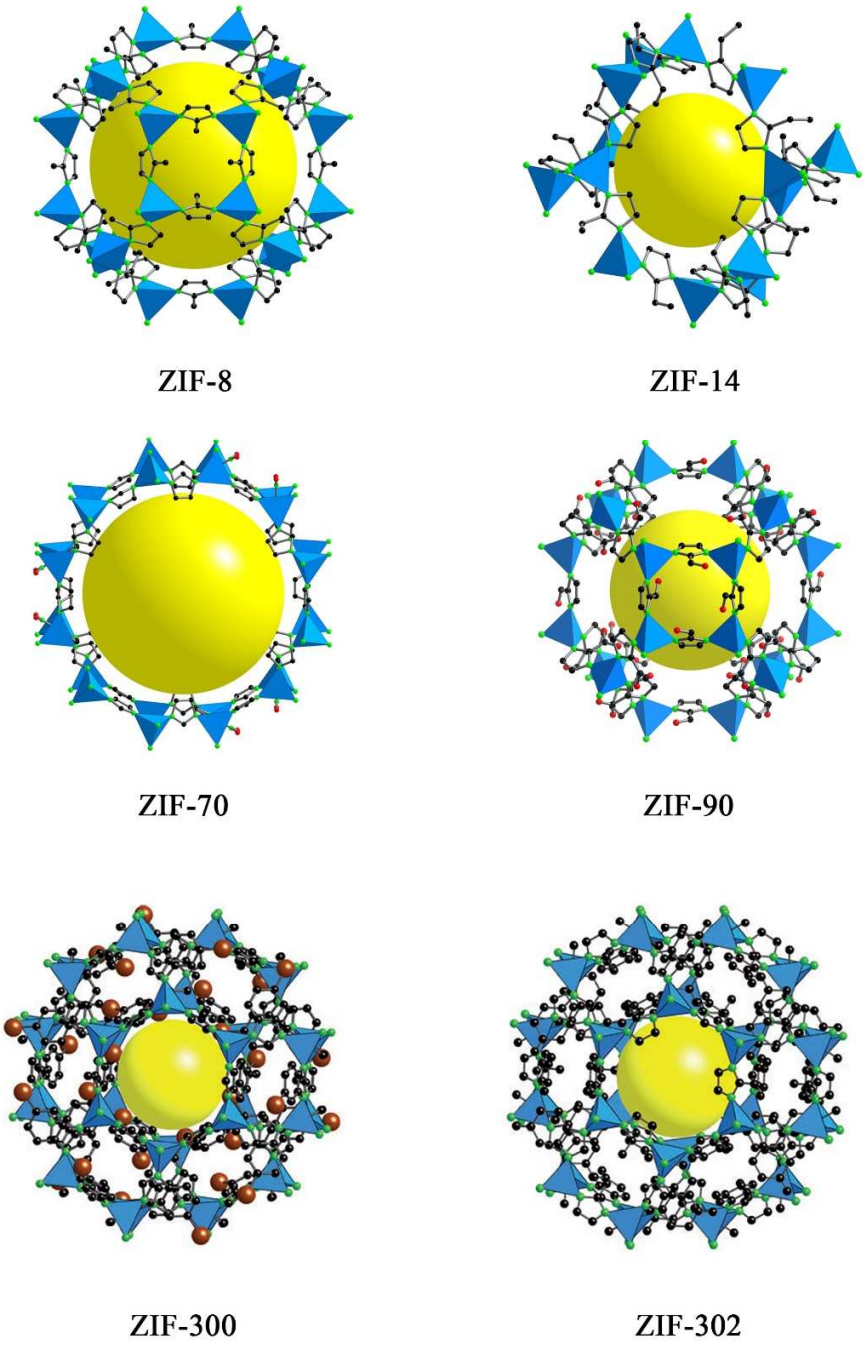

Figure 3 Crystal structure of different type of Zeolite imidazole Frameworks [24] [25]

1.3 Mixed Matrix Membranes MMMs:

Hybrid membranes consist of two parts. First part is a polymer matrix, and second part is an inorganic filler (silica, zeolite, MOFs, etc.). The main advantage of MMMs is combining both features of the matrix and filler, including mechanical properties, surface area, stability, and selectivity.

The fabrication of high performance MMMs relied on Different factors (suitable combination, particle size, particles agglomeration, interface morphology):

1- Polymer/inorganic filler combination, where this factor could play major role in controlling the performance of mixed matrix membranes.

2- Particle size of the filler. Synthesizing smaller particles leads to more interfacial area between polymer and filler, which will improve membrane performance. In addition, because of smaller particles, we can fabricate thinner membranes [19].

3- Agglomeration of filler particles as a result of difference in physical properties especially with higher loading of filler. This leads to formation of inhomogeneous particle distribution in polymer matrix, that cause MMM defects.

4- Interface morphology between polymer and filler in nanoscale. I tis crucial factor, and can affect transport properties. The ideal situation when there is a good adhesion between polymer and filler. There are other situations where interface voids; and solidification of the polymer happens that reflects in MMMs performance [26].

A detailed literature review discusses MMMs incorporated with metal organic frameworks in chapter two.

1.4 Objectives:

The main objectives of this research are:

1- Fabrication of highly selective mixed matrix membranes MMMs where a commercial polymer (polyimide PI) embedded with crystals filler of hydrophobic chabazite zeolite imidazole frameworks ZIFs (ZIF-300 and ZIF-302). First, ZIFs crystal will be synthesized by solvothermal method, that will be incorporated in the polymeric matrix, followed by membrane casting.

2- Characterization of synthesized ZIFs and MMMs using different characterization techniques. First, synthesized ZIF-300 and ZIF-302 will be investigated by (XRD, SEM, TGA, NMR, and gas sorption analysis) to explore the crystallinity, morphology, surface area, thermal, and chemical stability. Second, membranes (including pure, and MMMs) will be characterized with XRD, SEM, TGA, and sorption analysis.

3- Investigation of the effect of different loadings of the ZIFs filler on the selectivity and permeability of the resulting MMMs.

4- Study of the permeation performance of the fabricated membranes using fixed volume and variable pressure permeation method for single gas at dry conditions at 35 °C and 4 bar.

Chapter I:

A general introduction about global warming and its effects in the world, followed by the most recent technologies that are being used to control the emission of greenhouse gases especially for carbon dioxide. In addition, a review about metal organic frameworks and its applications in gas adsorption. Finally, an overview about mixed matrix membranes.

Chapter II:

A detailed literature review about developing a mixed matrix membrane for CO_2 separation by incorporating the metal organic frameworks and Zeolite imidazole frameworks (MOFs & ZIFs) in a polymer matrix. Exploring the previous works in the last decade to have a general scope about mixed matrix membranes MMMs and its use in separation gas mixtures.

Chapter III:

The methodology part will present the synthesizing steps of both ZIFs and MMMs, followed by the characterization techniques that will be used to explore the properties of ZIFs and mixed matrix membrane. Also, Permeation performance of the membrane will cover in this chapter.

Chapter IV:

This section will illustrate the results of both synthesizing and characterization part. In addition, the results of investigation different loading and conditions will include in this section. Finally, the experimental result of selectivity and permeability of CO_2 separation will be presented.

Chapter V:

Conclusion part will discuss the results that achieved in this study, followed by recommendations for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Mixed Matrix Membranes as a gas separation approach overcome the drawbacks of polymeric membranes by incorporation of inorganic filler such as MOFs in polymer matrix, which lead to remarkable enhancement in gas separation. Also, combing two material means gaining extraordinary material that has properties of both materials. Many studies conducted to illustrates the improvement in permeability of MMMs and selectivity toward a pure gas or gas mixture by adding an inorganic filler to polymeric membranes. The most general used polymers are polysulfone, Matrimid, Pebax, and PES. While the inorganic filler could be silica [27] [28], Zeolite [29] such as SAPO-34 [30], In addition, as its extraordinary properties, metal organic frameworks could be used as a filler in mixed matrix membranes. In this chapter, the most recent works in incorporation of MOFs with polymeric matrix will be presented, followed by the preparation methods of mixed matrix membranes, and the main factors that might affect properties and the performance of MMMs.

2.2 Literature Review

In this work Anjum et al. successfully developed a mixed matrix membrane where MIL-125 and NH_2-MIL-125 incorporated as a filler in Matrimid polyamide. It is reported that

the functionalization of MIL-125 played major role in enhancing the permeability and selectivity of the membrane compared with un functionalized MIL-125 and pare polymer, since the selectivity of amine group to CO_2 [31]. Also, they investigated the filler loading (5-30 wt%) effect toward selectivity and permeability, where the selectivity decreased with filler loading increment, due to interfacial voids formation between filler and polymer. However, the permeability increased with high loading. The selectivity for (CO_2:CH_4) was (44:50) for MIL-125 and NH_2-MIL-125 at 15 wt%.

Another study showed the positive effect of functionalization of MOFs in the permeability and selectivity. MIL-101(Cr) and sulfonated MIL-101(Cr) was incorporated with sulfonated poly (ether ether ketone) SPEEK, and separation performance of both membranes was tested [32]. The S-MIL-101 showed higher selectivity for CO_2/CH_4 and CO_2/N_2 (50 and 53) compared with unmodified one. In addition, they reported that humidification of membrane for one week before testing has major effect in increasing the permeability, that reached to 2064 Barrer for CO_2.

The first report shows increasing of permeability and selectivity simultaneous where Naseri and his group fabricated MMM using Matrimid and MIL-101 as a filler that shows high selectivity comparing with neat Matrimid in gas permeability measurements [33]. The best selectivity for CO_2/N_2 and CO_2/CH_4 were 53 and 56 respectively. Permeability for CO_2 and N_2 were 6.95 Barrer and 0.12 Barrer respectively at 10% loading of MOF. The permeation test operated at 10 bar and $35C^0$.

Other study introduced zeolite like MOFs (ZMOFs) another sub-class of metal organic frameworks that has anionic frameworks. Sod-ZMOFs embedded in Matrimid [34]. The

MMM prepared using solution casting method, and permeability measurement for pure and mixture gases were performed. The permeability of CO_2 and CH_4 increased while filler loading increase. However, the ideal selectivity slowly decreased comparing with bare Matrimid. On the other hand, the performance of MMM comparing with neat Matrimid for gas mixture was exhibited a good actual selectivity for CO_2/CH_4, that reached to 43.4 at 20% loading of sod-ZMOF. This showed the competitive adsorption mechanism between CO_2 and CH_4.

Gong and his group reported a mixed matrix membrane by incorporating SIFSIX-3-Zn MOF that fabricated by sonochemical method in a polyethylene oxide (XLPEO) to investigate the permeation measurement for binary mixture of CO_2/CH_4 and CO_2/N_2 [35]. Higher selectivity for CO_2/CH_4 achieved at 20 wt% loading of filler 30, with 590 CO_2 permeability. For CO_2/N_2 the selectivity was 29 at 10 wt% loading, and the permeability for CO_2 was 670. Increasing CO_2 permeability was attributed to the selective adsorption of CO_2 through the pores of MOF.

A study was reported to investigate the change of filler type, and operating conditions on the permeation measurement [36]. ZSM-5 and MIL-53 were used as a filler in Matrimid 5812. Adding ZSM-5 to matrix increase the permeability and decrease the selectivity. Also, formation of interfacial voids between filler and polymer led to clear decline in MMM performance as result of incompatibility between zeolite and polymer at high loading. On the other hand, MIL-53 was performed successfully due to breathing property of MIL-53, selective adsorption for CO_2 due to polar interaction, affinity of organic linker to matrix chains, and higher free volume formation, which reflected on the membrane separation performance. The selectivity increased from 14.8 to 23.6 at 15wt % of filler. In addition,

increasing the operating pressure will increase the selectivity of MMM, while a reverse result for increasing the temperature. Furthermore, in this study, mixture gas permeation was performed. The trend was the same but lower than pure gas measurements, because of presence of CH_4 and CO_2 in the mixture prevent more adsorption for CO_2, CH_4 also prevents the condensation of CO_2, Increasing the free volume due to polymer chain movement because of plasticization effect of CO_2 molecules, this will allow CH_4 diffuses through membrane.

Another comparative study for investigation of different type of MOFs as a filler in MMM was conducted by Feijani and his group [37]. CuBDC, CuBTC, MIL-53(Al), and modified MIL-53(Al) were embedded in Poly(vinylidene fluoride) (PVDF). The permeation measurements were proceeded for each type. All MMMs exhibited permeability and selectivity increment with filler loading except for PVDF-MIL-53 were a slight decrement in CO_2/CH_4 selectivity. Functionality and breathing behavior of MIL-53 were the main reasons of increasing permeation, while unoccupied Cu atom for CuBDC and CuBTC generate site for gas molecules.

NH_2-MIL-125/PSF performance for gas mixture (CO_2, CH_4: 50/50 mol%) also studied by Xisngyu Guo et al [38] which showed permeability enhancement compared with pure polysulfone. This study showed the major role of NH_2- functional group in improving the permeability due to its adsorption affinity and providing a transport channels for more gas molecules to pass through the membrane. In addition, pressure effect in the permeation were studied at 10 bar which showed a decline in permeability.

Salman Shahid & Kitty Nijmeijer [39] reported the Fe(BTC) MMM using Matrimid as a polymer matrix. This membrane showed high increasing in CO_2 permeability with MOF loading, because of high solubility and diffusion through MOFs. Also, CH_4 permeability increased slightly compared with CO_2. The ideal selectivity also increased slightly with MOFs loadings. The feed pressure also was investigated to show the trend of permeation performance with pressure, which showed decreasing in CO_2 permeability before the polymer plasticization, further increasing showed permeability enhancement due to solubility and diffusivity. In the other hand, CH_4 decreased with pressure increasing due to solubility coefficient.

Another mixed matrix membrane was fabricated using MIL-53/Matrimid for testing the single gas permeability and ideal selectivity [40]. This MMM showed high permeability for CO_2 and CH_4 at high loading, but the selectivity decreased at 20 wt.% because of void formation and particle agglomeration. The interaction between the CO_2 and MIL-53, and the affinity of MOF to polymer sustained in this good performance of this membrane.

A mixed matrix membrane of cubic-MOF-5/polyetherimide PEI was introduced to study separation performance [41]. Higher loading of filer increased the H_2 permeability, and selectivity. Solubility coefficient was a main role for CO_2 and CH_4 permeability whereas diffusion coefficient was facilitated N_2.

In addition, Zeolite imidazole frameworks ZIFs had been investigated as a filler in mixed matrix membranes. The most common type is ZIF-8 that has a good thermal, chemical, and hydrothermal stability. Shaid and his group studied particle fusion approach to fabricate

ZIF-8/Matrimid 5218 [42]. A better performance achieved with MMM compared with native polymer for CO_2/CH_4 mixture. They permeability increased with filler loading and the CO_2/CH_4 selectivity reached to highest value at 30 wt.%.

Another study where ZIF-8 with different metal ion (nitrate, acetate, chloride) at 30 wt.% were embedded in polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene SEBS co-polymer [43]. Interfacial free volume between the filler and matrix plus mass transfer resistance of MMM were the main reasons of high performance of this mixed matrix membrane. The general trend for permeability was increasing comparing with neat polymer, and the highest achieved CO_2/CH_4 selectivity was 5.4.

Zhao et all were synthesized a mixed matrix membrane of ZIF-8 and poly(vinylamine) (PVam) then coated by polysulfone PSf to investigate CO_2/N_2 mixed gas separation [44]. The permebilty and selectivity was significantly increased with high loading. They claimed that the main reasons were the 3.4 nm pore size plays the exclusion effect for any gas has high kinetic diameter. Also, the interaction between ZIF-8 and matrix chains which enhance the diffusion of gases through membrane. The effect of temperature and pressure was observed in this study which showed decline in permeability and selectivity for mixed matrix membrane.

A hollow ZIF-8 was incorporated into a co-polymer PVC-g-POEM [45]. The successful incorporation of filler was lead to high permeability for CO_2 with small decrement in selectivity of CO_2/CH_4. The main reasons for CO_2 permeability enhancement were first, chemical interaction between ether group (C-O-C) of POEM and CO_2 which increase the

solubility, second, gas exclusion explanation due to the pore size of h-ZIF-8, which increase the diffusivity. finally, the interaction between the ZIF-8 linker and CO_2.

Another study where Vajihah Nafisi & May-Britt Hagg developed a dual layer mixed matrix membrane of ZIF-8/PEBAX-2533 [46]. As reported the increasing filler loading increase the permeability for gases. However, the CO_2/CH_4 and CO_2/N_2 selectivity decreased. The effect of tow layer mixed matrix membrane and CO_2 capacity of ZIF-8 played major contribution in permeation performance.

A comparative study was conducted to investigate the separation performance of three MMM by using $Cu_3(BTC)_2$, ZIF-8, and MIL-53(Al) as a filler and Matrimid as a matrix. Two type of membrane were prepared (asymmetric and dense) using priming protocol synthesis [47]. Binary mixture of CO_2/CH_4 and CO_2/N_2 was introduced to measure the selectivity of the membrane. The affinity for polymer and kinetic diameter of CO_2 increased the permeance of CO_2 compared with other gases.

ZIF-71 was incorporated into 6FDA-Durene polyimide to study permeation performance of pure gases [48]. The permeability was increased with filler loading for all gases while dropping the selectivity. Gas diffusivity increased due to large pore cavity of ZIF-71.

Tao Li and his groups successfully prepared a selective mixed matrix membrane for CO_2 separation by embedding ZIF-7 as a filler in ploy(amide-b-ethylene oxide) Pebax 1657 on polyacrylonitrile support [49]. Chain solidification affected the permeability of MMM, while CO_2/CH_4 selectivity increased with filler loading because of solubility of CO_2 in polymer and the molecular sieving property of ZIF-7.

Table 2 Leiturature review for most recent works in MMM for CO_2 separation

Polymer	MOFs	Loading wt%	P (bar) T (C^0)	Conditions	P_{CO2} (Barrer)	P_{CH4} (Barrer)	P_{N2} (Barrer)	Selectivity CO_2/CH_4	Selectivity CO_2/N_2	Ref.
Matrimid 9725	-		9	Pure gas	6			30	-	[31]
Matrimid 9725	MIL-125	15			18			44	-	
Matrimid 9725	MIL-125	30			27			37	-	
Matrimid 9725	NH_2-MIL-125	15			17			50	-	
Matrimid 9725	NH_2-MIL-125	30			50			37	-	
SPEEK	S-MIL-101 (Cr)	40	1	Mixed gas	34/33			39	40	[32]
SPEEK	S-MIL-101 (Cr)	40		Pure gas, humidified	2064			50	53	
Matrimid 5218	-		10	Pure gas	4.44			35	34	[33]
Matrimid 5218	MIL-101	10			6.95			56	53	
Matrimid 5218	MIL-101	15			5.70			47	44	
Matrimid 5218	MIL-101	20			5.85			37	42	
Matrimid 5218	MIL-101	30			7.99			44	47	
Matrimid 5218	-		5		5.59			37.3		[34]
Matrimid 5218	Sod-ZMOF	5			6.83			36.2		
Matrimid 5218	Sod-ZMOF	10			7.54			35.8		
Matrimid 5218	Sod-ZMOF	20			12.17			32.9		
Matrimid 5218	-			Mixed gas	7.16			30.8		
Matrimid 5218	Sod-ZMOF	5			6.96			36.6		
Matrimid 5218	Sod-ZMOF	10			7.05			37.7		
Matrimid 5218	Sod-ZMOF	20			13.79			43.4		
Polyethylene oxide XLPEO	-		1, 25 C^0	Mixed gas	450	30		15		[35]
Polyethylene oxide XLPEO	SIFSIX-3-Zn	10			620	23		27		

Polyethylene oxide XLPEO	SIFSIX-3-Zn	20			590	20		30		
Polyethylene oxide XLPEO	SIFSIX-3-Zn	-			470		25		19	
Polyethylene oxide XLPEO	SIFSIX-3-Zn	10			670		23		29	
Polyethylene oxide XLPEO	SIFSIX-3-Zn	20			630		22		29	
Matrimid 5812	-		3, 35 C^0	Pure gas						[36]
Matrimid 5812	MIL-53	6			9	0.41		20.6		
Matrimid 5812	MIL-53	15			19	0.80		23.6		
Matrimid 5812	MIL-53	24			30	2.86		11.2		
Matrimid 5812	MIL-53	30			46	6.15		7.5		
Matrimid 5812	-			Mixed gas						
Matrimid 5812	MIL-53	6			8.1	0.43		19		
Matrimid 5812	MIL-53	15			17.6	0.88		20		
Matrimid 5812	MIL-53	24			27.5	3.06		9		
Matrimid 5812	MIL-53	30			41.8	7.58		5.5		
PVDF			5, 25 C^0	Pure gas	0.915	0.043	0.056	21.27		[37]
PVDF	CuBTC	5			1.067	0.043	0.058	24.81		
PVDF	CuBTC	10			2.002	0.048	0.059	41.70		
PVDF	CuBTC	15			3.206	0.080	0.089	40.07		
PVDF	CuBDC	5			1.126	0.043	0.059	26.18		
PVDF	CuBDC	10			1.602	0.045	0.061	35.60		
PVDF	CuBDC	15			1.987	0.044	0.060	45.15		
PVDF	MIL-53	5			1.210	0.057	0.074	21.22		
PVDF	MIL-53	10			1.553	0.074	0.096	20.98		
PVDF	NH_2-MIL-53	5			1.107	0.048	0.064	23.06		
PVDF	NH_2-MIL-53	10			1.406	0.054	0.072	26.03		
PSF			3, 30 C^0	Mixed gas	9.5	0.43	22			[38]
PSF	NH_2-MIL-125	10			18.5	0.65	28.3			

PSF	NH_2-MIL-125	20			29.3	0.99	29.5			
PSF	NH_2-MIL-125	30			40	1.37	29.2			
PSF			10, 30 C^0	Mixed gas	7.3	0.27	27			
PSF	NH_2-MIL-125	10			15	0.53	28.5			
PSF	NH_2-MIL-125	20			22.8	0.78	29.5			
PSF	NH_2-MIL-125	30			36.8	6.48	5.7			
Matrimid 5812			5,35 C^0	Pure gas	8.8	0.35		25		[39]
Matrimid 5812	Fe(BTC)	10			9.5	0.35		27		
Matrimid 5812	Fe(BTC)	20			11	0.37		27.25		
Matrimid 5812	Fe(BTC)	30			13	0.42		30		
Matrimid			3, 35 ^{0}C	Pure gas	6.2	0.22		28.2		[40]
Matrimid	MIL-53	5			6.8	0.23		29.6		
Matrimid	MIL-53	10			7.45	0.24		31		
Matrimid	MIL-53	15			12.43	0.24		51.8		
Matrimid	MIL-53	20			14.52	0.96		15.1		
PEI			6, 25 ^{0}C	Pure gas	1.68	0.09	0.1	18.67		[41]
PEI										

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